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14. ABSTRACT
The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

15. SUBJECT TERMS
corrosion protection, self-healing, coatings, polymers

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POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #3

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1 Summary

We successfully identified an effective anti-caking agent that will allow our microcapsules to be air dried without causing adhesion problems in the primer. We also identified new requirements for producing microcapsules with good shelf life (> 6 months) in the absence of a protective metal shell

2 Project Goals and Objectives

APL is ramping up activity to meet our first set project milestones in five months. The first set of milestones is to choose the best performing silane additive, the optimum silane concentration, and the optimum microcapsule/zinc powder ratio in the primer. We have ramped up our activity at APL and are currently waiting to have our subgrant in place with PPG.

3 Key Accomplishments

3.1 Anti-Caking Agent

Last month we discovered that nonionic surfactants could prevent irreversible caking of microcapsules during filtration, but that the leftover residue caused adhesion problems. The adhesion effects were not large when the microcapsules were used at small loading (<10%), but the potential for long-term water-assisted delamination was enough to raise alarm.

Turning to the food industry, a common anti-caking agent is silica powder. Also used to improve polymer strength and durability, silica would actually enhance the mechanical properties of the primer, and it would not be expected to affect adhesion. Numerous experiments have shown that silica powder not only prevents the powders from caking when they air dry, but it also generally improves filtration.

3.2 Reaction Rate and Curing Time

Since making the move to include zinc powder for galvanic protection, the need for the Ni:Zn microcapsule shell has come into question. Eliminating the Ni:Zn shell greatly reduces the cost and complexity of producing the microcapsules. However, the metal shell still provided two important functions: (1) improved mechanical durability and (2) a hermetic seal for better shelf life.

These two functions must be addressed in order to successfully transition to an all polymer shell. Such a transition would likely require a thicker shell, a shell with improved mechanical properties, or possibly a composite shell including some form of filler. Last month's experiments showed that some formulation changes were able to improve the speed of the reaction, but not without generally compromising the mechanical strength of the shells. Heating the existing recipe at 35°C for two hours provided the best balance of speed and performance.

Continued experiments have reinforced the prevailing view that the existing microcapsule recipe is difficult to improve upon. Recipes with faster reaction rates resulted in microcapsules that were not even suitable for vacuum filtration. Some small changes have provided clear benefits, however. For higher concentrations of octadecyltrimethoxy silane, polyphenylene isocyanate must be replaced with poly(hexamethylenediisocyanate) to improve solubility. One or the other must be included with isophorone diisocyanate to form tougher polymer shells. Silica nanopowder has also been added to improve filtration. We are currently investigating whether this material also incorporates into the polymer shell to create a harder material with improved barrier properties.

	% in 5g mixture; added to 30% Gum Arabic						% in 5g mixture; balance is Gum Arabic						Processing Notes			
	% SILANE		% MONOMERS				% CROSSLINKERS									
Date Made	OTS	MPTMS	IPDI	PPI	HMDI or PHMDI	TDI	DETA	PEI	ED	XD	Stir time	Heat after Stir?	Appearance after 1 hour	Can it be filtered after 24 hours (other time) with $C_{12}E_4$?	Liquid Center	Loose Powder
1/25/12	50		35			15	5	5			1 hr	35C 2hr	Glassy; but some internal polymerization; a couple shells look like "pacman"	Yes! **fastest filter time so far	Yes	No
1/26/12	50		45	5*	5		5	5			1 hr	35C 2hr	Less brittle looking, more rubbery; a couple look like "pacman"	No	Yes	No
2/2/12	50		40		10		5	5			1 hr	35C 3hr	Clumpy suspension after 2 hr heating; spheres look better than expected; lots of liquid; look like	Yes but slow	Yes	No
2/2/12	45		50	5			5	5			1 hr	35C 2hr	Shells are fairly thick; more internal polymerization than desired; 2 hrs may be too long; repeat @ 1 hr	Yes, not as fast as expected given	Yes	No
2/3/12	45		50	5			5	5			1 hr	35C 2hr	more liquid than 2h sample; best time for PPI samples	Yes (3 days)	Yes	No
2/3/12	50		45		5 (P)		5	5			1 hr	35C 2hr	glassy; breaks are clean"	Yes (3 days), slower than the PPI	Yes	No
2/7/12	50		40		10 (P)		5	5			1 hr	35C 1hr	smooth glassy; breaks are not as clean as the 5%	washed w/ H_2O in sep funnel; added	Yes	"sticky" powder
2/7/12	50		40		5 (P)	5	5	5			1 hr	35C 1hr	more dimpled/rubbery; cracks don't break;	washed w/ H_2O in sep funnel; added	Yes	No
2/14/12	65		25		5(P)	5	5	5			1 hr	35C 1hr	glassy; crack with pressure; lots of liquid	washed w/ H_2O in sep funnel; filtered	Yes	No
2/14/12	75		20			5	10	10			1 hr	35C 2hr	glassy, but shells are fragile	washed w/ H_2O in sep funnel; filtered	Yes	No
2/16/12	0		90	10			5	5			1 hr	35C 30min	Made a 20g batch; Added 2g nano SiO_2 prior to adding crosslinkers;	Filtered half on 2/15 with the	Yes (& Yes)	No (& Yes)
2/20/12	0		70			30	5	5			1 hr	35C 2hr	Brittle shells crush with pressure	Filtered half on 2/23; filtered last		
2/20/12	0		90		10 (P)		5	5			1 hr	35C 2hr	Glassy; shells crack with pressure	Attempted to filter half with 1g SiO_2	X	X
2/21/12	0		90		10 (P)		5	5			1 hr	35C 2hr	Added 2g SiO_2 nanopowder prior to adding crosslinkers; Lots of excess SiO_2, shells have	Filtered half on 2/23; not super	No/Yes	No/Yes
2/23/12	65		25		10 (P)		5	5			1 hr	35C 2hr	Added 2g SiO_2 nanopowder prior to adding crosslinkers; glassy, but a little more brittle than			
2/24/12	65				5 (P)	5	5	5			30 min	35C 2hr	Added 2g SiO_2 nanopowder prior to adding crosslinkers; glassy			
2/24/12	45		50	5			5	5			30 min	35C 2hr	Added 2g SiO_2 nanopowder prior to adding crosslinkers; glassy			

Table I: *List of experiments tried to improve the reaction speed for microcapsule formation.*

Given that we do not expect great improvements in reaction speed, we next set out to determine the minimum reaction time for obtaining microcapsules that can survive filtration. Figure 1 shows that the minimum time is approximately 5 days. The sample on the left is a dense cake cured for 2 days, and the sample on the right is from the same batch but allowed to cure for 6 days. Note how the 6-day batch is already breaking up before any agitation. The 2-day batch is typical for weaker microcapsules, which rupture solely under the pressure of filtration. From past experience, microcapsules that survive filtration also survive spray painting.

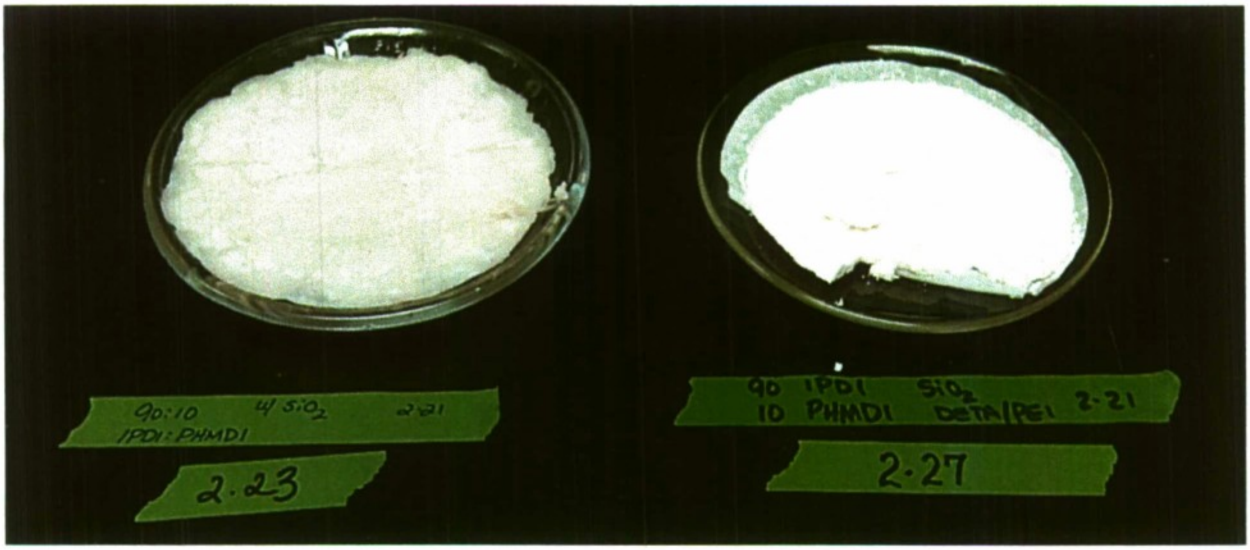

Figure 1: *Comparison of microcapsules filtered from the same batch after 2 days (left) and 6 days of curing (right). Note how the 6-Day sample scatters much more light, indicative of internal porosity between the dry microcapsules, and has already begun to break up into a loose powder without any external agitation.*

3.3 Shelf Life without Metal Shell

Since the hermetic seal was one of the primary functions of the metal shell, it will be important to assess the impact of removing the shell on shelf life. To this end, we investigated polymer microcapsules using thermogravimetric analysis (TGA). We compared two samples made in July and August of last year with a newer sample made in December (Figure 2). The two older samples had 35% solids and 47% solids, respectively. The latter microcapsule had been heat treated to 40°C, which caused unwanted internal polymerization. This internal polymerization (free floating polymer) means that not all of the 47% polymer can be attributed to the outer shell. The August microcapsule was synthesized at room temperature and is more representative of the high performing microcapsules.

The newer sample from December was also synthesized at room temperature. It also contained 35% polymer. 35% polymer appears to be the minimum requirement for generating strong microcapsules that survive filtration. Note that 35% is higher than the previously recommended 20% that was used when plating with metal. The added bulk appears to be necessary for filtration, and it probably assists in shelf life. Although we have no data from the August batch when it was originally made, it is encouraging that it retained the same liquid fraction as the newer batch from December.

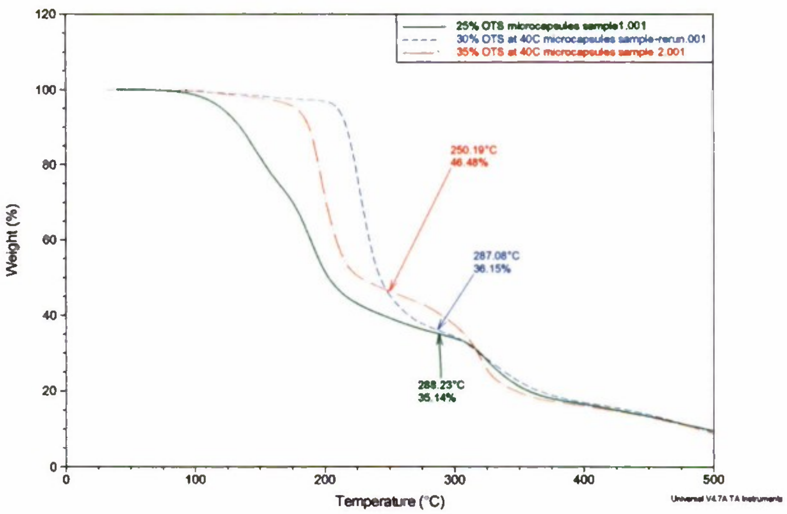

Figure 2: *Thermogravimetric analysis of polymer microcapsules synthesized in July (red), August (blue), and December (green). The higher solids content for the July sample is attributable to the elevated temperature at which it was originally synthesized. The 35% solids from the other two samples is more indicative of the polymer shell thickness needed to form durable microcapsules with good shelf life in the absence of a metal shell.*

4 Next Steps

4.1 Performance Optimization

The recent improvements in microcapsule processing will be meaningless unless they are matched by equally large improvements in corrosion protection. APL will therefore shift its strategy to focus solely on optimizing the corrosion protection of the primer through its self-healing capability.

We will apply the lessons from the last two months to our new processing protocol, and it will remain fixed. We are currently synthesizing microcapsules with different combinations of silane and silane concentration to be used in test panels for corrosion testing next month.